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Determination of Total Gaseous Nonmethane Organic Emissions as Carbon: Summary of Comments and Responses for Method 25

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Research Triangle Park, NC

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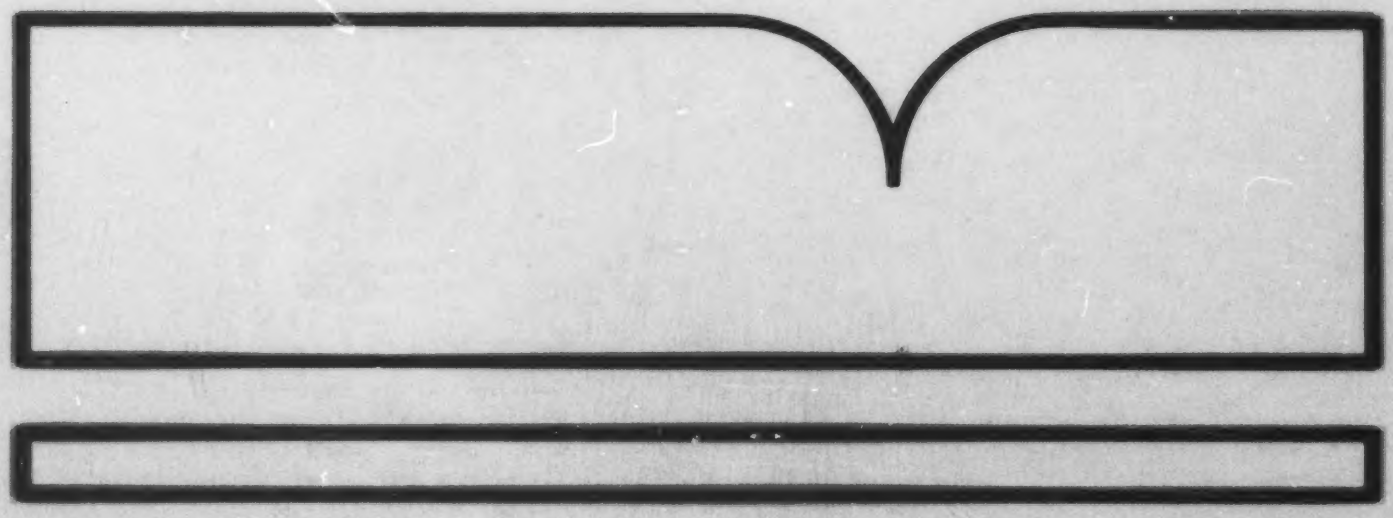

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This is a summary of the comments received on the proposal of the revised Method 25 (51 FR 40448) and the Agency's responses.

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DETERMINATION OF TOTAL GASEOUS NONMETHANE ORGANIC EMISSIONS AS CARBON

SUMMARY OF COMMENTS AND RESPONSES

Emission Measurement Branch

Emission Standards and Engineering Division

U.S. Environmental Protection Agency

Research Triangle Park, North Carolina 27711

August 1987

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Table 1. LIST OF ACRONYMS USED

EPA	- Environmental Protection Agency
VOC	- Volatile Organic compounds
NSPS	- New Source Performance Standards
QA	- Quality Assurance
VOC	- Volatile Organic Compounds

Chapter 1

INTRODUCTION

On November 7, 1986, the U.S. Environmental Protection Agency (EPA) published in the Federal Register (51 FR 40448) the revised Method 25, "Determination of Total Gaseous Nonmethane Organic Emissions as Carbon." This method was proposed under the authority of Sections 101, 111, 114, 116, and 301 of the Clean Air Act, as amended.

Public comments were solicited at the time of proposal. To provide interested persons the opportunity for oral presentations of data, views, or arguments concerning the proposed revisions of the test method, a public hearing was scheduled for December 22, 1986, at the Research Triangle Park, North Carolina, but no person desired to make an oral presentation. The public comment period was from November 7, 1986, to January 21, 1987.

Three comment letters were received concerning issues relative to the proposed test methods. A detailed discussion of these comments and responses is summarized in this document. The comments have been carefully considered, and appropriate changes have been made in the proposed revision.

Chapter 2

SUMMARY OF CHANGES SINCE PROPOSAL

The following changes have been made in the revised method since proposal:

1. Section 4.1.1 has been added to include a contamination check of the sampling equipment.

2. Section 4.1.2 has been revised to allow the use of a vacuum gauge in place of a mercury manometer for measuring system pressure in the field.

3. Section 4.1.4 has been revised to reduce the leak check period from 10 to 5 minutes.

Chapter 3

SUMMARY OF COMMENTS AND RESPONSES

Commenter IV-D-1

1.1 Comment: Although it was not the intent of the writers of the method that it be applied universally to any source emitting volatile organics, past practice has shown that State and local regulatory agencies, and even the EPA, will adopt the method without regard for its limited applicability. Thus, it behooves the EPA to write reference methods that have applicability beyond a narrow scope of specific sources. An arbitrary method with diminished value should be avoided.

For the method to be applicable to a wide range of sources not covered by new source performance standards (NSPS), or studied during the development of these changes, the method should be written in the form of general guidelines. These would take the form of a stringent quality assurance (QA) program to insure acceptable performance for the sources to be sampled. The changes in the method needed to make it applicable to specific sources would then be sanctioned, rather than have poor or meaningless data delivered with a rigid procedure. Thus, much data already collected using variations of the present Method 25 will maintain its validity.

Response: We agree that it was not our intent that the method be applied universally to any source emitting volatile organic compounds (VOC). We also agree that it would be beneficial if the method could be written to have a broad applicability to all types of sources, but we do not agree that this should be done at the expense of the method's accuracy and precision at those sources for which it is the compliance test method.

Our experience with performance guidelines for Method 25 is that they would become so cumbersome that the method would not be useable for routine testing. However, this does not preclude any individual or organization from performing the necessary testing to demonstrate that their procedures or equipment are adequate for the requirements of Method 25.

Commenter IV-D-1

1.2 Comment: The intent of the filter system is to remove condensible organic and other particulate material from the sample gas. The filter temperature was chosen to correspond to the filter temperature of EPA Method 5, which was selected to prevent collection of sulfuric acid mists on the filter and has nothing to do with photochemical reactivity of volatile organic materials. This arbitrary filter temperature should be replaced with one consistent with removal of condensible organics or particulate that does not react photochemically to form ozone.

Some organic compounds that condense in the atmosphere and, therefore, do not react photochemically, pass through a filter at 250°F and are measured by the method. This biases the measurement to the high side. These materials should be excluded from the sample. We suggest that the filter temperature be reduced to 190°F. Even at this temperature, some nonphotochemically reactive condensible organic materials will pass the filter and be measured, but the potential problem of the sample gas temperature falling below the dew point will be avoided.

There is no need for the Method 25 filter temperature to correspond to that of Method 5. There is no relationship between organic emissions and particulate emissions. Each test method reports its results in units that are not comparable. If the agency wants to measure the condensible

organic material in the emissions, it should designate a method designed to do so. There are satisfactory methods in use for this purpose that could be appropriated. We suggest the Oregon Department of Environmental Quality Method 7.

Response: We do not agree that all photochemically reactive organic compounds must be gases at ambient temperatures. Even those compounds that are normally liquids at ambient temperature may have a significant vapor pressure and thus exist partly in the gas phase as evidenced by the evaporation of organic liquids stored in open containers. If the filtration temperature were reduced from 250°F to 190°F, we believe that compounds that should be counted as VOC would be artificially excluded from the sample.

Commenter IV-D-1

1.3 Comment: The filtering system could be greatly simplified and the oven design improved. The design of these components should not be rigidly specified such that possible improvements are precluded. For example, the solvents used to clean the probe and filter system between samples should be thoroughly removed before assembly of the equipment to preclude contamination of the sample. The long purge time could then be eliminated. As another example, it would be desirable to reduce the volume of the filtering system so that the error in sample volume would then be less than 1 percent. The filter system volume could be reduced further by using 1/8-inch tubing throughout except for thermocouple wells. A 3/8-inch filter holder can be constructed of Swagelok parts. This would eliminate the need for a quarter of the equipment that would be hauled to the sampling site. Lastly, we see no need for an elbow in the probe.

Response: There is no requirement in the method to clean the probe and filter system between samples so this was not a factor in determining the length of purge time. The purge time of 10 minutes was chosen to insure that the sampling system was thoroughly purged with sample gas and at equilibrium and does not seem excessive. Since there is a sample purge before sampling begins, there is no error in sample volume and the volume of the filtering system is not critical.

The elbow at the end of the probe allows the opening of the probe to be pointed away from the direction of sample gas flow to reduce the amount of particulate matter entering the sampling system.

Commenter IV-D-1

1.4 Comment: The leak check can be reduced from 10 minutes to 5 minutes. For a probe system with 0.1 liters volume, a sample size of 3 liters, and a leak rate of 1 percent, the pressure would change 19 mm in 5 minutes. Reducing the probe system volume would reduce the time needed to conduct the leak check. It should be noted that a leak can be detected in the same manner by pressurizing the system, with the added advantage that in the event of a leak, its location can be easily found by wetting the component connections and looking for bubbles.

Response: We agree that the leak-check procedure can be reduced from 10 minutes to 5 minutes. The method has been revised to reflect this.

While a leak check could be conducted under positive pressure, it is more appropriate to conduct the leak check under vacuum which is how the sample train would be operated while collecting the sample.

Commenter IV-D-1

1.5 Comment: The proposed sampling procedure ignores the need for isokinetic sampling if particulate is present. If the stack temperature is less than the filter temperature, condensed organic material, if present, will be disproportionately sampled. If the stack temperature is greater than the filter temperature, a nonisokinetic sampling system can be used.

A lower filter temperature would reduce the need for isokinetic sampling. The filter temperature would be lower than the stack temperature in more situations. Also, errors induced by nonisokinetic sampling when the filter temperature is greater than the stack temperature would be reduced because the difference in temperature would be smaller and the amount of particulate volatilized in the sampling train would be less.

Response: We believe that isokinetic sampling is not necessary because particles formed by condensation are typically submicron in size and will behave as a gas. Thus, even if the sample is not collected isokinetically, it will not contain a disproportionate amount of condensed organic matter.

Commenter IV-D-1

1.6 Comment: Mercury manometers are not suitable for field use. A vacuum gauge is suitable to estimate vacuums in the field. The initial and final tank pressures can be measured before leaving and upon return to the laboratory. We routinely hold evacuated sample tanks for several weeks without experiencing even small leaks.

Response: We agree that a vacuum gauge of sufficient accuracy would be suitable to measure vacuum in the field. The method has been revised to reflect this.

Commenter IV-D-1; Commenter IV-D-2

1.7 Comment: A post-test leak check should not be eliminated. A post-test leak check is necessary to assure sample integrity. If the promulgated method incorporates the elaborate filter system, a post-test leak check will be even more of a necessity considering the number of connections suggested in the proposal.

Response: At the beginning of the run, the system vacuum is at its highest and the potential for leaks is greatest. This is the most critical time for leak checking the sampling train. If no leaks are detected at this point, it is very unlikely that any would develop during sampling. At the end of the sampling period, the vacuum remaining in the cylinder will be near zero and the potential for leaks in the system will be very low. Also if a post-test leak check were added, it would lengthen the time required to complete a test and would be very unlikely to add any additional information.

1.8 Comment: A trap burnout temperature of 200°C is specified by the proposed method. This temperature may suffice for the more volatile solvents. However, in some sources, specifically some for which there are no NSPS, organic material captured in the cryogenic trap may pyrolyze rather than vaporize at these temperatures and will not be recovered.

To insure complete removal of organic material, the traps should be heated to 600°C. At this temperature, carbon residuals left by pyrolysis of heavy organics are burned to carbon dioxide and removed from the trap. The EPA chose the 200°C trap heating temperature out of fear from CO_2 would diffuse through the stainless steel trap at higher temperatures and

contaminate the sample. We have never had a problem from CO_2 diffusing into the traps at 600°C trap heating temperatures. Our experience was that trap blanks of less than 5 ppm were readily achieved at the 600°C temperature, even when the trap was bathed in CO_2 from an acetylene torch EPA's own studies did not indicate a problem with CO_2 diffusion into the trap when heated to 600°C.

Response: Because the sample is filtered at 121°C, all materials reaching the condensate trap must be a gas at that temperature. We believe that a material which can exist as a gas at 121°C will be vaporized easily when heated to 200°C. At the same time, a temperature of 200°C should be low enough to avoid decomposing the sample during the vaporization process. Thus, the 200°C temperature was chosen because it provided a temperature that was high enough to vaporize the sample while minimizing any problems due to decomposition from temperatures that are too high. Diffusion of CO_2 through stainless steel at high temperatures was not a factor in choosing a heating temperature.

Commenter IV-D-1

1.9 Comment: Materials other than chromia on alumina are superior catalysts. An oxygen donating catalyst such as manganese dioxide, should be allowed so that when more organics are present than oxygen is available, the catalyst will provide the additional oxygen required to convert all of the organic carbon to carbon dioxide.

The EPA contractor developing this method evaluated manganese dioxide as an oxidation catalyst but found it unacceptable. However, the

contractor evaluated the catalyst at an inappropriate operating temperature (454°C). The chromia on alumina also failed to perform adequately at this temperature. When operated at the proper temperature (650°C), manganese dioxide is a superior catalyst to chromium on alumina because of its oxygen donating properties.

The manganese dioxide catalyst does degrade at temperatures above 700°C. Thus, proper temperature control is necessary.

Chromia on alumina tends to spread the peaks. Sharper peaks from the chromatography can be obtained with manganese dioxide. The EPA contractor reported a peak asymmetry factor of 1.38 for the chromia on alumina catalysts. The National Council of the Paper Industry for Air and Stream Improvements, Inc. found a peak asymmetry of 1.24 for the manganese dioxide catalyst. A factor of 1.0 indicates asymmetrical peak, and is preferred. The sharper peaks allow for more accurate determination of the concentrations.

Use of an oxygen donating catalyst alleviates the need for adding oxygen or air to the carrier gas prior to the oxidation catalyst, thus simplifying the analysis system. It avoids an additional hazard in the work place. There is sufficient oxygen in the sample air to regenerate the catalyst upon each injection. We have used a manganese dioxide catalyst for several years without regeneration with air other than that in the sample. We believe that the manganese dioxide catalyst should be specified, or at least be allowed, provided that the QA portion of the method is satisfied.

Response: Although there is good evidence that manganese dioxide based catalysts have limited ability to oxidize organic compounds in an

oxygen-poor environment, this alone does not solve the problem of catalyst overloading. There is also evidence that, in the absence of sufficient oxygen, some of the organic material is converted to carbon which deposits on the surface of the catalyst and is subsequently converted to carbon dioxide when sufficient oxygen is present. It appears that this process does not always go to completion and may, over a period time, lead to loss of oxidation efficiency. Even though manganese dioxide has the ability to donate oxygen for oxidation in an oxygen poor environment, it would still be necessary to add auxiliary oxygen to ensure good performance with samples having high organic levels. Thus, it's ability to donate oxygen does not give it any special advantage over other catalysts.

Although most people who use manganese dioxide catalysts operate them at 850°C, the manufacturers of two of the most widely used manganese dioxide-based catalysts recommend that they be operated at temperatures no higher than 454°C. This is the temperature at which they were operated in our tests, as well as 850°C.

Even though manganese dioxide may have shown a slightly lower asymmetry factor than that of chromia on alumina, the difference is not significant. As a result of our evaluation, we concluded that chromia on alumina represented the best choice of a catalyst considering all the factors that affect a catalyst's performance.

Commenter IV-D-1

1.10 Comment: Our experience with nickel reduction catalysts is that they fail rapidly. Any sample containing sulfur compounds poison the catalyst. We have used a rhodium catalyst on a variety of sources with no degradation. We have not replaced our reduction catalyst in 7 years of

continual service. We suggest that the rhodium catalyst be specified or at least be allowed provided that the QA portion of the method is satisfied.

Response: We would not expect to collect sulfur containing compounds from sources where Method 25 is specified as the compliance test method. We did not evaluate rhodium as a reduction catalyst and could not specify it as the reduction catalyst for Method 25. However, the rhodium catalyst could be approved as an alternative if sufficient data were presented to support its use.

Commenter IV-D-2

2.1 Comment: The proposed method does not address the problem of residual contamination in the sampling train which users of Method 25 have confirmed to be a serious problem. A laboratory confirmation of the presence of residual contamination from a previous test or laboratory contamination needs to be specified. The proposal should incorporate a pretest conditioning and QA check of the sampling equipment which will contribute to the overall reliability of Method 25. Such a procedure could consist of baking the probe and trap assembly while purging with a suitable organic-free gas and performing an analysis on the trap and sample tank.

Response: We agree that such a procedure should be included in Method 25. We have revised the method to incorporate a contamination check.

Commenter IV-D-2

2.2 Comment: The proposed particulate filtration system is unnecessarily complex since particulate concentrations from applicable

sources are generally very low. Retrofitting the sampling system to incorporate this elaborate filtering system is estimated (by EPA in 1985) to cost approximately $1,700. Although we agree that a filtration system is needed, we believe that an in-stack filter (as mentioned in the proposal as an option when electrical systems are prohibited) would be adequate. By using an in-stack filter, the probe, from the back half of the filter holder to the condensate trap, could then be baked along with the trap to determine the condensible organics as in the present system. The method could alternatively allow the more elaborate filtration system for problem sources.

Response: We believe that an in-stack filter system is appropriate only at those sources where a heated out-of-stack filter would be prohibited for safety reasons. Because many organic compounds can change physical state between ambient temperature and 250°F, the temperature at which the sample is filtered determines whether some organic compounds are counted as VOC or not. Under these circumstances, we believe that the only equitable way to measure VOC emissions is to filter all samples at the same filtration temperature regardless of the source's operating temperature.

Commenter IV-D-2

2.3 Comment: The tolerances established by EPA for QA appear to be very stringent for such a complex analytical system. Although we have had limited experience with the system, we are concerned with the achievability of the proposed accuracy standards. We believe the present standards are adequate and should be maintained.

Response: Our laboratory program to revise the method demonstrated that the tolerances proposed in the revised method should be achievable by any well operated system. Relaxing the tolerances would be likely to increase the incidence of poor laboratory practice which would result in a decline in the overall precision of the method.

Commenter IV-D-3

3.1 Comment: The proposed addition of a heated filter and the associated filter heating equipment should be optional rather than mandatory. In many cases, it is known prior to sampling that no particulate matter is present in the stack gas. In such a situation, the requirement of a heated filter adds unnecessary equipment which would increase maintenance costs and sampling time.

Response: Even in stack gases which should be free of particulate matter, our experience shows that the method will yield acceptable precision only when the sample is filtered. It is extremely sensitive to contamination - 100 μg of extraneous carbon in the sample would be measured as about 30 ppm of VOC. One of the best ways to insure that contaminant carbon is not included in the sample is to prevent it from entering the sample train by filtering the sample.

Table 2. LIST OF COMMENTERS

Docket Number A-86-05

Docket Item Number	Commenter/Affiliation
IV-D-1	John E. Pinkerton, Manager Air Quality Program National Council of the Paper Industry for Air and Stream Improvement, Inc. 260 Madison Avenue New York, New York 10016
IV-D-2	Ben A Brodovicz, Chief Division of Technical Service and Monitoring Department of Environmental Resource Commonwealth of Pennsylvania Post Office Box 2063 Harrisburg, Pennsylvania 17120
IV-D-3	U.V. Henderson, Associate Director Environmental Affairs Research and Environmental Affairs Department Post Office Box 509 Beacon, New York 12508